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IN THE UNITED STATES PATENT  
AND TRADEMARK OFFICE

Applicant(s): Eiki YASUKAWA et al.

Serial No. : 10/606,706

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For : NON-AQUEOUS ELECTROLYTE AND LITHIUM SECONDARY  
BATTERY USING THE SAME

Art Unit : 1745

Examiner : MERCADO, JULIAN A

Hon. Commissioner of Patents  
and Trademarks  
Washington, D.C. 22313-1450

DECLARATION UNDER 37 CFR 1.132

S I R :

I. Yasuyuki SHIGEMATSU, a citizen of Japan, who declares and says that:

I am an inventor of the present U.S. Patent Application as identified above and understand the English language. I studied the Official Action dated July 12, 2006 received in said application, and in order to prove that the present invention is not obvious over the references cited by the Examiner, the following experiments were carried out under my supervision.

II. Experiments

[Non-aqueous electrolyte 3 (Examples 26 and 27)]

In non-aqueous solvents comprising a chain state phosphate (a1) and a cyclic carboxylate (b1) and having a predetermined volume ratio between the chain state phosphate (a1) and the cyclic carboxylate (b1) shown in Table 3 below,

were individually dissolved a predetermined amount of a vinylene carbonate compound (c1) and a vinylethylene carbonate compound (c2), predetermined amounts of a cyclic amide compound (d1), a cyclic carbamate compound (d2), and a heterocyclic compound (d3), and a lithium salt as a solute were dissolved individually to prepare non-aqueous electrolytes 3 in Examples 26 and 27 having a solute concentration of 1 mol/dm<sup>3</sup>. On the other hand, the non-aqueous electrolytes in Comparative Examples of Examples 26 and 27 are non-aqueous electrolytes which do not contain either of the vinylene carbonate compound (c1) or the vinylethylene carbonate compound (c2). Next, with respect to each of these electrolytes, a self-extinguishing property (flame retardancy) and a conductivity were measured. The results are shown in Table 4 below.

Table 3

	Electrolyte			Additive			
	Solute	Solvent	Volume ratio	Kind	Amount Formulated (wt%)	Kind	Amount Formulated (wt%)
26	LiBF <sub>4</sub>	DEMP+GBL	25:75	VEC+VC	8+2	NVP	5
27	LiBF <sub>4</sub>	DEMP+GBL	40:60	VEC+VC	8+2	NMC	5
Com. 1 of 26	LiBF <sub>4</sub>	DEMP+GBL	25:75	VEC	8	NVP	5
Com. 2 of 26	LiBF <sub>4</sub>	DEMP+GBL	25:75	VC	2	NVP	5
Com. 1 of 27	LiBF <sub>4</sub>	DEMP+GBL	40:60	VEC	8	NMC	5
Com. 2 of 27	LiBF <sub>4</sub>	DEMP+GBL	40:60	VC	2	NMC	5

"Com." in the above table means "Comparative".

Meanings of abbreviations used in Table 3 are the same as mentioned on page 46 of the present specification.

Next, using the non-aqueous electrolytes shown in Table 3, coin-form secondary batteries were produced in the same manner

as mentioned on page 47 of the present specification. The obtained positive electrode sheet was die-cut into a piece having a diameter of 12.5 mm to form a positive electrode.

A battery was produced in the same manner as mentioned on page 47 of the present specification.

Using the coin-form battery produced, the charge-discharge efficiency of a battery was measured in the same manner as mentioned on page 47 of the present specification.

In addition, the cycle characteristics of discharge capacity retaining ratio were obtained by further repeating the above charge-discharge cycle. The discharge capacity retaining ratio was determined from the following formula.

Discharge capacity retaining ratio (%)  

$$= \{(\text{Discharge capacity in the } n\text{-th cycle}) / (\text{Charge capacity in the First cycle})\} \times 100$$
 (wherein n represents the number of cycles)

Table 4

	Self - extinguishing property (sec)	Conduc- tivity (mS/cm)	First-cycle charge-discharge characteristics		Third-cycle charge-discharge characteristics	
			Discharge capacity (Ah/kg)	Charge- discharge efficiency (%)	Discharge capacity (Ah/kg)	Charge- discharge efficiency (%)
26	within 1 sec	6.8	156	74.4	157	99.2
27	within 1 sec	7.0	150	71.8	148	98.4
Com. 1 of 26	within 1 sec	6.9	145	68.0	143	97.7
Com. 2 of 26	within 1 sec	6.8	130	61.3	111	91.9
Com. 1 of 27	within 1 sec	7.0	135	63.3	130	97.7
Com. 2 of 27	within 1 sec	7.0	104	47.3	101	98.3

As can be seen from Table 4, non-aqueous electrolyte 3 of the present invention has excellent flame retardancy and conductivity as compared with the electrolytes in which either of the vinylene carbonate compound (c1) or the vinylethylene carbonate compound (c2) is not contained, and further excellent charge-discharge characteristics and cycle characteristics can be achieved.

[Non-aqueous electrolyte 4 (Examples 34 and 36)]

In non-aqueous solvents using a chain state phosphate (a1) and a cyclic carboxylate (b1) or a cyclic carbonate (b2), and having a predetermined volume ratio shown in Table 5 below, predetermined amounts of a vinylene carbonate compound (c1) and a vinylethylene carbonate compound (c2), and a lithium salt as a solute were dissolved individually to prepare non-aqueous electrolytes 4 in Examples 34 and 36 having a solute concentration of 1 mol/dm<sup>3</sup>. On the other hand, the non-aqueous electrolytes in Comparative Examples of Example 34 are non-aqueous electrolytes which do not contain either the vinylene carbonate compound (c1) or the vinylethylene carbonate compound (c2). Next, with respect to each of these electrolytes, a flash point and a conductivity were measured. The results are shown in Table 6 below.

Table 5

	Electrolyte			Additive			
	Solute	Solvent	Volume ratio	Kind	Amount formulated (wt%)	Kind	Amount formulated (wt%)
34	LiPF <sub>6</sub>	TMP+GBL	80:20	VC	5	VEC	5
36	LiPF <sub>6</sub>	TFEDMP+GBL	80:20	VC	2	VEC	8
Com. 1 of 34	LiPF <sub>6</sub>	TMP+GBL	80:20	VC	5	None	-
Com. 2 of 34	LiPF <sub>6</sub>	TMP+GBL	80:20	None	-	VEC	5

Meanings of abbreviations used in Table 5 are the same as mentioned on page 51 of the present specification.

Then, using the non-aqueous electrolytes shown in Table 5, coin-form secondary batteries were produced. With respect to each of the secondary batteries produced, charge-discharge characteristics were measured. The results are shown in Table 6. The method for producing a secondary battery, and the methods for evaluation of charge-discharge capacity and charge-discharge efficiency were the same as those for the secondary batteries produced using the non-aqueous electrolytes 3.

Table 6

	Flash Point (°C)	Conduc- tivity (mS/cm)	First-cycle charge-discharge characteristics		Third-cycle charge-discharge characteristics	
			Discharge capacity (Ah/kg)	Charge- discharge efficiency (%)	Discharge capacity (Ah/kg)	Charge- discharge efficiency (%)
34	None	6.7	145	69.7	144	98.1
36	None	5.9	144	64.6	134	96.4
Com. 1 of 34	None	6.8	0	0	0	0
Com. 2 of 34	None	7.0	104	47.3	101	98.3

As can be seen from Table 6, the non-aqueous electrolytes in Comparative Examples of Example 34 have no flash point, but they are disadvantageous in that a high discharge capacity cannot be obtained and the charge-discharge efficiency is low. In contrast, the electrolytes in Examples 34 and 36 are advantageous not only in that they have no flash point, but also in that excellent charge-discharge characteristics can be obtained.

[Anode material using graphite carbonaceous material (A) and

carbonaceous material (B)]

(Electrochemical evaluation of electrode)

With respect to the electrode materials, electrochemical properties were measured by a charge-discharge test.

A negative electrode was prepared as mentioned on pages 55 and 56 of the present specification.

(Example 39)

Non-aqueous electrolyte of Example 39 having a solute concentration of 1 mol/dm<sup>3</sup> was prepared in the same manner as mentioned on pages 56 to 58 of the present specification.

On the other hand, the non-aqueous electrolytes in Comparative samples of Example 39 are non-aqueous electrolytes which do not contain either of the vinylene carbonate compound (c1) or the vinylethylene carbonate compound (c2) of the present invention.

The compositions of the electrolytes and the powder physical properties parameters of the anode materials are shown in Table 7, and the results of evaluations are shown in Table 8.

Table 7

	Electrolyte			Additive			
	Solute	Solvent	Volume ratio	Kind	Amount formulated (wt%)	Kind	Amount formulated (wt%)
39	LiPF <sub>6</sub>	TMP+GBL+EC	60:20:20	VC	2	VEC	5
Com. 1 of 39	LiPF <sub>6</sub>	TMP+GBL+EC	60:20:20	VC	2		
Com. 2 of 39	LiPF <sub>6</sub>	TMP+GBL+EC	60:20:20			VEC	5

Meanings of abbreviations used in Table 7 are the same as

mentioned on page 60 of the present specification.

Table 8

	Flash point (°C)	Conductivity (mS/cm)	First-cycle charge-discharge characteristics	
			Discharge capacity (Ah/kg)	Charge-discharge efficiency (%)
39	None	6.7	335	88.0
Com. 1 of 39	None	6.8	73	31.8
Com. 2 of 39	None	6.7	284	86.0

As can be seen from Table 8, the non-aqueous electrolytes and anode materials in Comparative Examples have no flash point and thus have nonflammability. However, the resultant batteries exhibit less capacity, and hence they insufficiently function as a battery. On the contrary, the non-aqueous electrolyte and anode material of Example 39 are advantageous not only in that they have no flash point, but also in that excellent charge-discharge characteristics can be obtained.

### III. Conclusion

As shown in Tables 4, 6 and 8, by using (a) at least one phosphate selected from (a1) a chain state phosphate and (a2) a cyclic phosphate; (b1) a cyclic carboxylate; (c1) a vinylene carbonate compound and (c2) a vinylethylene carbonate compound in combination, excellent results can be obtained.

That is, the non-aqueous electrolyte of the present invention is advantageous not only in that it has flame retardancy (self-extinguishing property) or nonflammability (has no flash point), but also in that it has extremely high conductivity.

I believe that the above effects would be indeed surprising and could never be expected from the descriptions of the cited references.

IV. I further declare that all statements made herein of my own knowledge are true and that all statements made in information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001, of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Dated: Oct 05, 2006

Yasuyuki Shigematsu

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